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APPLICATION OF PATENT OF INVENTION

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(60) References to other national related documents:

(71) Applicant(s): MEYNIER Claude - FR and  
TARRADE Jean-Luc - FR.

(72) Inventor(s): MEYNIER Claude and TARRADE Jean-Luc.

(73) Owner(s):

(74) Attorney(s): Harlé & Phellp Law Office

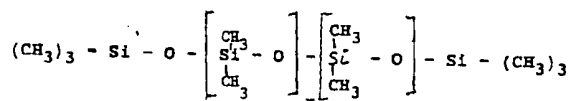
(54) Protective varnish with external anti-adherent surface.

(57) The invention subject is a protective varnish with  
external anti-adherent surface containing a synergic amount  
of:

(a) low viscosity aliphatic polyurethane resin;

(b) acrylic polymer in solution having molecular  
weight of about 100,000;

(c) modified silicone with molecular weight ranging  
between 2,500 and 4,500 and formula:



the weight ratio of (a) : (b) : (c) being about 90 : 1 : 0.5.

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The present invention relates to a protective varnish with external anti-adherent surface, especially a mono-component varnish without solvent.

Such varnish has multiple applications, for example, it can be used as anti-graffiti preventive product, as product preventing boat hulls or floating pontoons from collecting algae and sea-shell, as product for waxing the ski, as protective product for any surface against the risk of being bonded, as corrosion inhibitor of metallic surfaces, as protective agent against humidity and the like.

Product according to the present invention is a varnish having excellent adherence during its application to supports such as concrete, bricks, rocks, wood, stucco, metals, plastic materials. In addition, it has excellent anti-adhesion properties once the film is dry.

Such protective varnish needs only one simple application in most case because it is a mono-component product requiring no blending before hand.

As it is known to date, there is no mono-component protective varnish without solvent, which cannot be destroyed, even partially, when the graffiti is cleansed.

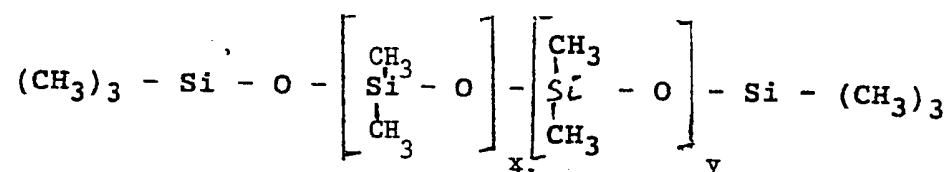
Varnishes of the prior art are usually multi-component products with or without solvent especially implying the use of solvent.

Patent application FR-A-86 01 852 describes a protective coating with external anti-adherent surface, made up with a combination of at least one aliphatic polyisocyanate, at

Since many years ago, there was a need of having a mono component varnish without solvent, which can be directly applied to a surface to be protected without prior blending.

The present invention meets this need by proposing a protective varnish with external anti-adherent surface containing a synergic amount of:

- (a) low viscosity aliphatic polyurethane resin;
- (b) acrylic polymer in solution having a molecular weight of about 100,000;
- (c) modified silicone with molecular weight ranging between 2,500 and 4,500 and having the formula:

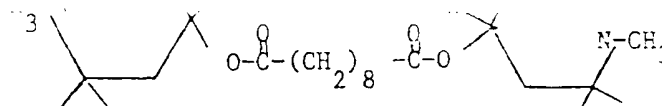


wherein R is an alkyl radical containing from 1 to 20 carbon atoms.

Weight ratio of (a) : (b) : (c) being about 90 : 1 : 0.5.

The present invention also relates to the hereafter characteristics considered solely or with all their technically possible combinations:

- the protective varnish is a mono-component product having a surface tension lower than  $20 \cdot 10^{-3}$  N/m especially about  $17 \cdot 10^{-3}$  N/m;
- the aliphatic polyurethane resin contains from 15% to 28% of isocyanate groups;
- the aliphatic polyurethane resin has a molecular weight of about 50,000;
- the radical R is a methyl radical;
- the varnish also includes talcum;
- the varnish also comprises an amine of formula:



- in addition, the varnish comprises a montmorillonite type clay;
- the varnish comprises, in addition, a paratoluene sulfonyl isocyanate;
- in addition, the varnish comprises a waterless emulsion in propylene glycol of a polysiloxane copolymer with molecular weight of about 80,000;
- the protective varnish also comprises tin dibutyldilaurate;
- talcum is used with a rate of 4 to 5% of the protective varnish composition total weight;
- amine of the tetramethyl piperidine family is used with the rate of 0.5 to 1% of the varnish composition total weight;
- pre-frozen clay is used with the rate of 1 to 2% of the varnish composition total weight;
- paratoluene sulfonyl isocyanate is used with the rate of 0.5 to 1% of the varnish composition total weight;
- polysiloxane copolymer is used with the rate of 0.3 to 0.6% of the varnish composition total weight;
- tin dibutyldilaurate is used with the rate of 0.2 to 0.6% of the varnish composition total weight;

The varnish contains:

• aliphatic polyurethane resin.....	89.70%
• talcum .....	4.49%
• amine of the tetramethyl piperidine family .....	0.90%
• clay .....	1.79%
• modified silicone.....	1.00%
• paratoluene sulfonyl isocyanate.....	0.72%
• tin dibutyldilaurate .....	0.45%

Total: ..... 100.00%

- the varnish is applied with a thickness of about 80  $\mu$ ;
- the varnish is used as preventive anti-graffiti varnish;

The present invention is illustrated without being limited by the manufacturing process and the packaging of protective varnish with reference made to annexed drawing wherein:

Figure shows the typical infra-red spectrum of acrylic polymer in use, the molecular weight of which is about 100,000.

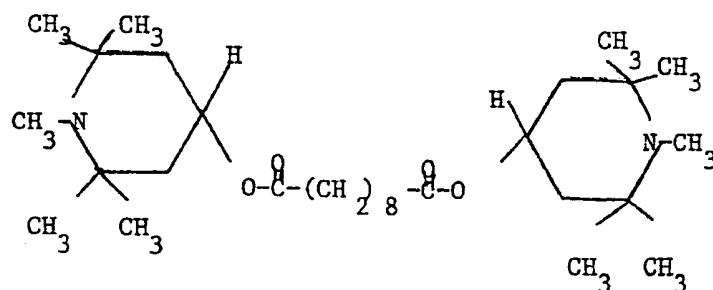
In a separated vat, pre-frozen the montmorillonite type clay is prepared with 15% in xylene using a deflocculating machine. This product is intended to adjust the final varnish consistency. It allows one to suppress run-out and breakdown. It improves the pore plugging quality of the final varnish. It is used with the rate of 1.79% of the varnish composition total weight.

The low viscosity aliphatic polyurethane resin is poured into a principal vat, this resin comprises about 22% of isocyanate groups and has a molecular weight of about 50,000. The amount in use is 89.70% by weight of the varnish composition total weight. Then, 4.49% by weight of talcum with respect to the total composition weight are added until obtaining a total dispersion with the help of the deflocculating machine. Talcum in use is blended with magnesium silicate and aluminum silicate. This component allows one to obtain a more or less mat varnish depending on the amount in use. As example, it is possible to introduce it with an amount from 1 to 15% by weight with respect to the total weight of the protective

while with a content of 15%, the film is mat.

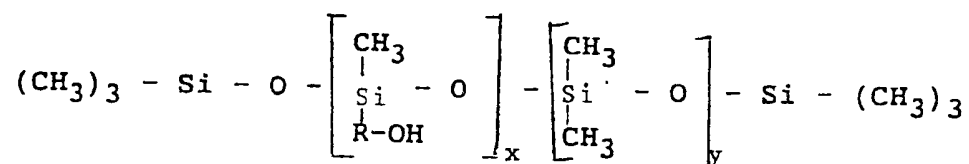
Pre-frozen clay of the separated vat is added to the main vat and the mixture is stirred until disappearance of curds.

Then, 0.72% by weight of paratoluene sulfonyl isocyanate is added to the vat, this addition allows one to neutralize the water contained in other components of the varnish. The composition is stirred from 5 to 10 minutes. After that, amine of the tetramethyl piperidine is added, this amine has the formula:



which is an anti-ultraviolet product stabilizing the light and allowing one to avoid cracking, fissuration, yellowing and other surface phenomena due to UV radiation.

This product is added with the rate of 0.90% by weight. Also, modified silicone having the formula below is incorporated into the composition:



wherein R is an alkyl radical containing from 1 to 20 carbon atoms.

This product allows one to lower the dry film surface tension. It improves surface

ADDITIONAL INFORMATION: POLYMERIZATION OF THE EMULSION

Then, the waterless emulsion is added to propylene glycol of the polysiloxane polymerized in the presence of a catalyst of the type of a tin compound.

This product prevents the foam formed during the varnish application from being stabilized. It destroys the air located between the support and the film and, improves the surface state of the dry varnish. It is used with a rate of 0.50% by weight of the protective varnish composition. Then the acrylic polymer solution is incorporated into the composition, the solution is characterized by its infra-red spectrum as it is illustrated in the figure and by its molecular weight of about 100,000. Its role is to improve the spreading and surface state properties. It allows one to avoid the foam formation on the protective varnish surface. It is used with the rate of 0.45 part by weight of the protective varnish composition.

Finally, the operation is ended with the addition of tin dibutyldilaurate which is used as catalyst for the reaction. Tin dibutyldilaurate allows one to accelerate the polyurethane formation and therefore to reduce the product drying time. It is used with the rate of about 0.45% by weight of the composition.

Before each new addition, it is suitable to ensure that the previous material is well homogenized.

All these operations are performed under controlled humidity and temperatures.

Hereafter, characteristics of the invention product are described:

Presentation: It is a mono-component product requiring no preparation nor blending to be done before the application. It is colorless, its aspect is satin, its hardness medium supple, its density at 20°C is 1.08 g/ml. Dry extract is from 94 to 96% by weight, its viscosity is ranging between 130 to 180 mPa.s, its flash point is 180°C in closed cup. It is applied with the rate of 200 g/m<sup>2</sup> at a temperature higher than 10°C and, it requires a drying time without

suitable to wait for a minimum of 2 hours between the application of each layer and a maximum of 4 hours. The product is packaged in metallic pots of 1, 5 and 25 kg. Its shelf life in closed pot is 8 months.

Varnish of the present invention, due to its very low surface tension is roughly lower than  $20 \cdot 10^{-3}$  N/m and, especially of  $17 \cdot 10^{-3}$  N/m, is a very efficient anti-graffiti preventive product.

However, it also favors the penetration of objects in water or in air by reducing the friction resistance. Applied on wood or on plastic materials, it allows a better gliding of boats, water-skis, sailing boards, etc. It reduces the collection of algae and sea shell of boat hulls or floating pontoons and, it facilitates the cleansing of immersed material. It advantageously replaces the usual ski waxing and, improves the sliding of luges, bobsleighs, etc. It also allows one to avoid the accumulation of snow on the roofs.

Varnish of the invention also is used for protecting all surfaces against the risk of been bonded by preventing the surfaces from undesirable posters. On the other hand, the varnish of the invention ensures an excellent protection against corrosion of metallic surfaces. It protects surfaces of rocks, concrete, stucco, etc. against humidity, while leaving the support breath. This varnish is air permeable and water impermeable.

In general, it is important that it is applied on perfectly clean and dry surfaces, in order to conserve all its properties.

Varnish of this invention is applied without any particular preparation of the support, in fact, it is enough that the support is dry and clean.

supple for applications on deformable surface.



Moreover, it is translucent (mat, satin or glossy) and, it allows one to conserve the support aesthetic.

Finally, varnish of the present invention may be considered as a protection against physical, chemical, atmospheric, etc. aggressions. In this meaning, it is considered as a product for surface treatment.

In the case of use of the protective varnish as anti-graffiti varnish, applied graffiti, regardless of their origin, is eliminated from the varnish using a sponge soaked with a cleansing agent.

Tests have shown that it is possible to perform more than 20 cleaning cycles without damaging the varnish nor its anti-adherent properties.

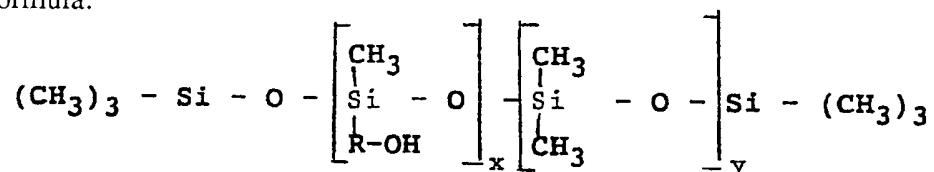
It is obvious for the man of the art that protective varnish of the present invention may be applied with brush, roller or even by projection on any appropriate painted or non-painted surface.

## CLAIMS

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1. Protective varnish with external anti-adherent surface, characterized by the fact that it contains a synergic amount of:

- a) low viscosity aliphatic polyurethane resin;
- b) acrylic polymer in solution having molecular weight of about 100,000;
- c) modified silicone with molecular weight ranging between 2,500 and 4,500 and the formula:



wherein R is an alkyl radical containing from 1 to 20 carbon atoms.

The weight ratio of (a) : (b) : (c) being about 90 : 1 : 0.5.

2. Varnish according to claim 1, characterized by the fact that it is mono-component product having a surface tension lower than  $20 \cdot 10^{-3}$  N/m.

3. Varnish according to any one of claims 1 or 2, characterized by the fact that it has a surface tension of  $17 \cdot 10^{-3}$  N/m.

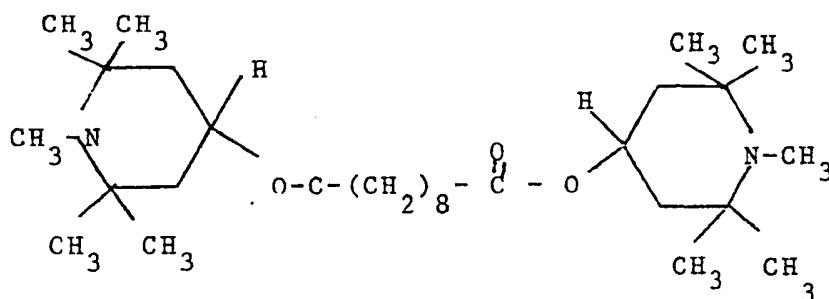
4. Varnish according to any one of claims from 1 to 3, characterized by the fact that the aliphatic polyurethane resin contains from 15 to 28% of isocyanate groups.

5. Varnish according to any one of claims from 1 to 4, characterized by the fact that the aliphatic polyurethane resin has a molecular weight of about 50,000.

6. Varnish according to any one of claims from 1 to 5, characterized by the fact that R is a methyl radical.

7. Varnish according to any one of claims from 1 to 6, characterized by the fact that

it also contains an amine of formula:



9. Varnish according to any one of claims from 1 to 8, characterized by the fact that it contains, in addition, clay of the montmorillonite type.

10. Varnish according to any one of claims from 1 to 8, characterized by the fact that it also contains a paratoluene sulfonyl isocyanate.

11. Varnish according to any one of claims from 1 to 10, characterized by the fact that it contains, in addition, a waterless emulsion in the propylene glycol of a polysiloxane copolymer having molecular weight of about 80,000.

12. Varnish according to any one of claims from 1 to 11, characterized by the fact that it also contains tin dibutyldilaurate.

13. Varnish according to any one of claims from 1 to 12, characterized by the fact that

- the talcum is used with the rate of 4 to 5% of the varnish composition total weight,
- the amine of tetramethylene piperidine family is used with the rate of 0.5 to 1.0% of the varnish composition total weight,
- the pre-frozen clay is used with the rate of 1 to 2% of the varnish composition total weight,

the polysiloxane copolymer is used with the rate of

- the polysiloxane copolymer is used with the rate of 0.3 to 0.6% % of the

the polysiloxane copolymer is used with the rate of

- the tin dibutyldilaurate is used with the rate of 0.2 to 0.6% % of the varnish composition total weight,

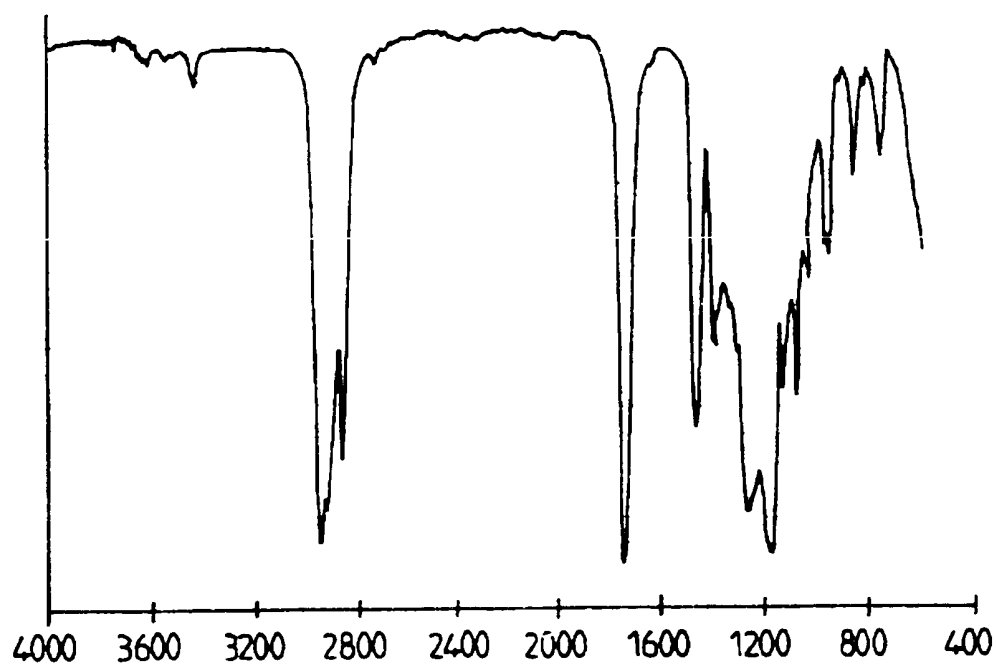
14. Varnish according to any one of claims from 1 to 12, characterized by the fact that it contains:

- aliphatic polyurethane resin .....	89.70%
- talcum .....	4.49%
- amine of the tetramethylene piperidine .....	0.90%
- clay .....	1.79%
- modified silicone .....	1.00%
- paratoluene sulfonyl isocyanate .....	0.72%
- polysiloxane copolymer .....	0.50%
- acrylic polymer .....	0.45%
- tin dibutyldilaurate .....	0.45%

Total: .....100.00%

15. Application of the varnish according to any one of claims from 1 to 14 as anti-graffiti preventive product.

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**SEARCH REPORT**  
established with the last claims deposited before  
the search begins

National Registration No.

FA 461555  
FR 9111158

DOCUMENTS CONSIDERED AS RELEVANT		Related claims of the examined application	
Category	Citation of document, with indication, where appropriate, of the relevant parts		
A	EP-A-0 293 084 (LORD) * page 4, line 11 - page 6, line 12 - claims 1-3 *	1	
A	EP-A-0 443 144 (BAYER) * page 2, line 55 - page 5, line 27 - claims 1, 2: examples 1-15 *	1, 7, 10	
A	WORLD PATENT INDEX Week 8029, June 7, 1980 Derwent Publications Ltd., London, GB; AN 80-50978C & JP-A-55 075 419 (NIPPON PAINT) * summary *	1	
A	US-A-4 369 300 (CARTER ET AL.) * column 1, line 48 - column 4, line 25; claims 1-12 *	1-20	
A	FR-A-2 630 353 (JIVAL) * claims 1-5 *	1-15	
			SEARCHED TECHNICAL FIELDS (Int.Cl. <sup>5</sup> )
			C08G C09D B05D
Search completion date		Examiner	
April 29, 1992		Bourgonie A F	

- Documents are classified as follows:
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